Feb 2nd, 8:00 AM - 12:30 PM

Toward Unraveling the Mechanisms of "Green" Mechanochemical Reactions

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Toward unraveling the mechanisms of "green" mechanochemical reactions

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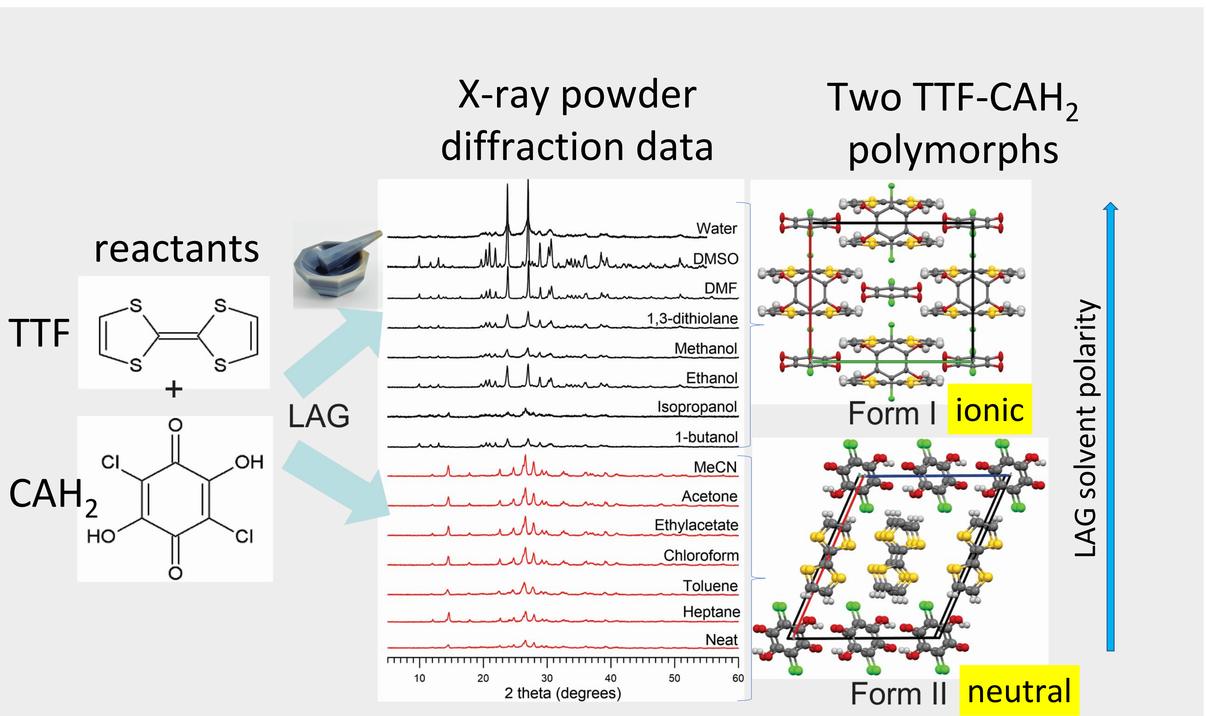
1 Project-related previous studies

Mechanochemistry affords "green" synthetic routes avoiding or reducing the use of reaction and crystallization solvents, thus providing environmentally friendly and cost-effective synthetic alternatives for many materials.

The solid-state reactants (typically powders) are usually ground together with small quantities of organic solvents, this is synthetic method is called **liquid assisted grinding (LAG).** Example:



LAG selectively leads to particular crystal structures (polymorphs) of the products (studied using X-ray powder diffraction), depending on the quantities and physicochemical properties of the liquids (water or organic solvents) used during grinding.

Not only for TTF-CAH_2, but in the synthesis of other two charge transfer complexes (CTC) of tetrathiafulvalene (TTF), TTF-CA[1] and TTF-DDQ[2] polar solvents (with high dielectric constant) are required for the formation of ionic polymorphs.

2 The scientific problem and the hypothesis

The overall features of the mechanochemical reaction mechanisms are poorly understood, and the reasons underlying the above liquid roles in LAG are unknown.

From our previous studies[1,2] the LAG solvents (the liquid phase with its physicochemical properties) seem required by the reaction mechanisms leading to ionic CTC, otherwise neutral or pseudo-neutral products are obtained.

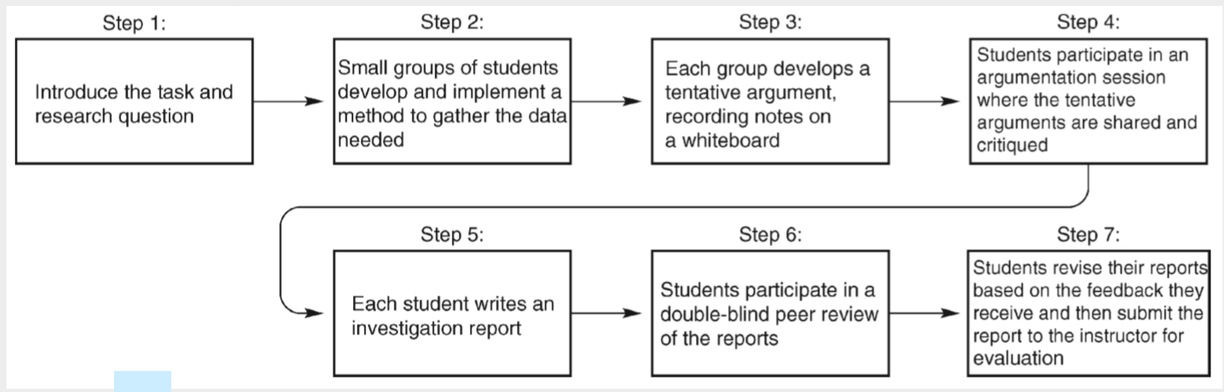
Toward gathering information that affords a better understanding of the reaction mechanisms, we are interested in measuring the reaction rate laws, for the LAG conditions leading to ionic and neutral CTC.

The hypothesis to test in this project is whether the polar solvents used in LAG must be present in the rate law for the mechanochemical reaction conditions yielding ionic products, or not.

3 PURS project objectives

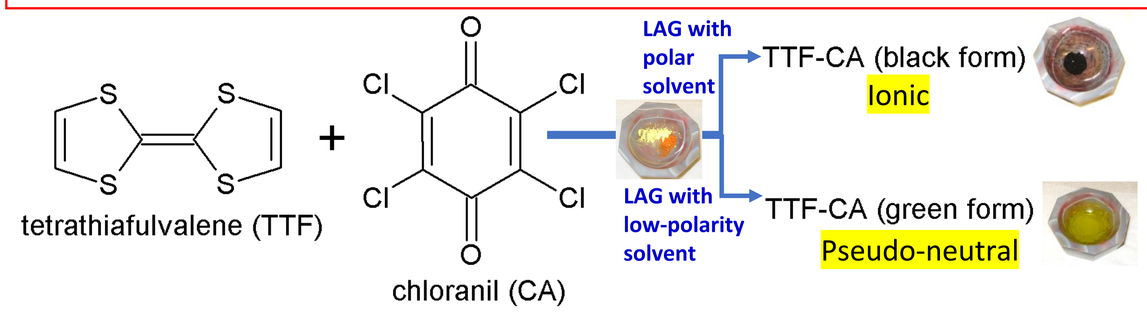
(1) To test an experimental method to study the kinetics of two (if possible four) mechanochemical reactions of synthesis of organic CTC, using laboratory X-ray powder diffraction.
(2) To determine the rate laws and the orders of the reaction (n, p, q) with respect to each reactant and the LAG liquid.
(3) To determine whether polar LAG liquids must be present in the rate laws for the conditions leading to ionic products, or not.
(4) To provide research experience to two undergraduate students. The **argument driven inquiry (ADI) instructional method**[3] will be used.

The seven steps of the ADI method[3]:

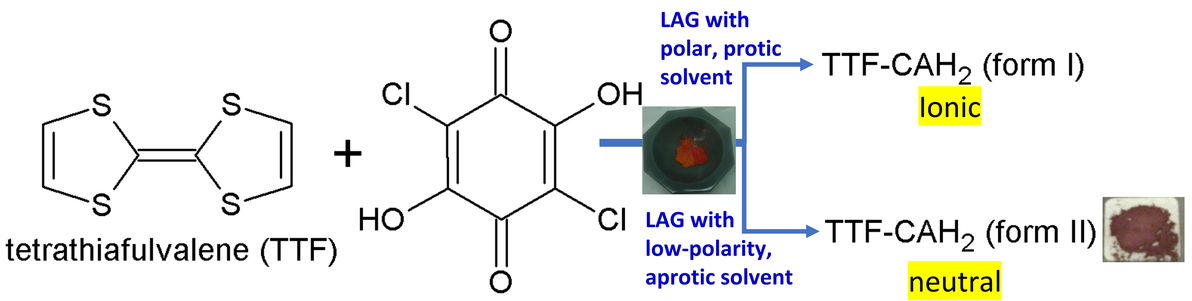


4 Methodology

Our research question: **Which are the rate laws for the following mechanochemical reactions?**



Rate law = $k\,\chi_{TTF}^{n}\chi_{CA}^{p}\,\chi_{LAG\ solvent}^{q}$; n, p and q must be experimentally determined.



Rate law = $k\,\chi_{TTF}^{n'}\chi_{CAH2}^{p'}\,\chi_{LAG\ solvent}^{q'}$; n', p' and q' must be experimentally determined.

- Laboratory X-ray powder diffraction will be used to determine quantitatively the amounts of crystalline and amorphous products and reactants after a fixed reaction time (*e.g.,* 5 min).
- Student-led argumentation sessions[3] will be carried out every 2-3 weeks, to analyze the experimental data collected and plan new experiments.
- Students will practice keeping a laboratory notebook and will prepare and peer-review project reports.
- The results will be shared at the VAS Fall Undergraduate Research Conference.

5 The significance of the results

- An experimental method to measure reaction rates using laboratory X-ray powder diffraction will be defined and tested. Optimally, it will be suitable to study other mechanochemical reactions.
- q and q' values will be used to understand the solvent role in the above reactions, and to demonstrate that the liquids and their physicochemical properties (*e.g.,* polarity) must be present during grinding, so that a reaction mechanism leading to ionic polymorphs is enabled. In absence of those liquids, pseudo-neutral or neutral products are obtained, and that will most likely involve differences in the rate laws measured.

References

(1) Saul H. Lapidus, Amit Naik, Alex Wixtrom, Nestor E. Massa, Vinh Ta Phuoc, Leire del Campo, Sébastien Lebègue, János G. Ángyán,Tarek Abdel-Fattah and Silvina Pagola. *Cryst. Growth Des.* 2014, **14**, 91−100.
(2) Sahnun Mohamud, Vinh Ta Phuoc, Leire del Campo, Néstor E. Massa, Silvina Pagola. *Synthetic Metals* 2016, **214,** 71–75.
(3) Joi Phelps Walker, Victor Sampson and Carol O. Zimmerman, *J. Chem. Educ.* 2011, **88**, 1048–1056.